On the Determination of the Critical Volume

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1892 Proc. Phys. Soc. London 12 137

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The constants for the formula $D = A + \alpha t$ are :—

Substance.	A.	α .
Methyl Formate . . .	·5025	—·0007155
Methyl Acetate . . .	·4839	—·0006740
Ethyl Formate . . .	·4759	—·0006490
Ethyl Acetate . . .	·4644	—·0006250
Methyl Propionate . . .	·4721	—·0006210

The critical densities of the five esters, obtained by the method of diameters, are :—

Methyl Formate	·3494
Methyl Acetate	·3255
Ethyl Formate	·3232
Ethyl Acetate	·3081
Methyl Propionate	·3123

From the differences between the observed and calculated mean densities it may be concluded that, though there may be in some cases a slight indication of curvature, it is far too small to affect the determination of the critical densities of these substances.

VI. *On the Determination of the Critical Volume.*

By SYDNEY YOUNG, D.Sc., *University College, Bristol*.*

ABOUT a year ago I read a paper before the Physical Society † on the “Generalizations of Van der Waals regarding Corresponding Temperatures, Pressures, and Volumes;” and at the close of the paper, after calling attention to the extreme difficulty attending the determination of the critical volume, I described a method by which the relative critical volumes of various substances could be ascertained. At that time it appeared to me that the direct determinations of the critical volumes of benzene, fluorbenzene, chlorobenzene, and acetic acid were probably approximately correct; and I was supported in this view by the fact that the ratios of the observed volumes

* Read October 28, 1892.

† Proc. Physical Soc. vol. xi. p. 233.

to that of fluorbenzene were practically identical with the ratios obtained by the graphical method then described.

I therefore assumed that the observed critical molecular volume of fluorbenzene was correct, and calculated the volumes of the other substances from their ratios to that of fluorbenzene, and gave these values as the probable critical molecular volumes of the other eleven substances. It was observed, however, that the critical volumes of the three alcohols and of ether obtained by this method were considerably lower than those previously deduced by Dr. Ramsay and myself, and were also lower than those calculated by M. Guye (*Compt. Rend.* cxii. p. 1257). Finally, I pointed out that if these values are taken as correct it would appear that the ratio of the actual critical density to the theoretical (for a "perfect" gas) is for many substances about 4·4.

Since then, M. E. Mathias has shown (*Compt. Rend.* cxv. p. 35) that the critical densities of the substances referred to in my paper may be determined by the method described by MM. Cailletet and Mathias (*Compt. Rend.* cii. p. 1202, civ. p. 1563). The method has also been found by M. Amagat to give excellent results with carbon dioxide, and by Mr. G. L. Thomas and myself with five of the lower esters; and I have therefore much pleasure in acknowledging the correctness both of the method (except, perhaps, in the case of the alcohols) and of the critical densities calculated by M. Mathias, and I have no hesitation in accepting these values in place of those previously adopted.

I have myself made an independent calculation of the critical densities of the twelve substances by this method, and the results I have obtained are practically identical (except in the case of the alcohols) with those given by M. Mathias.

The law of MM. Cailletet and Mathias may be described very briefly as follows:—The means of the densities of any substance in the state of liquid and of saturated vapour, when mapped against the temperature, fall on a straight line. I quite agree with M. Mathias that in the great majority of cases the verification of the law is perfect; but with the three alcohols, especially methyl alcohol, there appears to me to be very decided curvature, too pronounced to be neglected,

and I think it must be admitted that these substances behave exceptionally in this as in many other respects.

M. Mathias admits that at low temperatures the alcohols cease to follow the law ; but he is satisfied with the agreement between the observed and calculated mean densities for a range of 200° from the critical point. The constants employed by M. Mathias for ethyl alcohol can be ascertained from his paper, and I give below the mean densities calculated from these constants, together with those calculated from the observed molecular volumes given in my paper (*loc. cit.*).

The constants for the formula $D=A+at$ are:—

$A = \cdot 4149$, $a = -\cdot 0005576$, $t = \text{temperature (Centigrade)}$.

Means of Densities of Liquid and Saturated Vapour.

Temperature, Centigrade.	Observed.	Calculated.	$\Delta \times 1000.$
22·4	·3937	·4024	+87
39·45	·3865	·3929	+64
65·75	·3749	·3782	+33
89·7	·3636	·3649	+16
105·55	·3560	·3560	0
128·1	·3442	·3435	— 7
144·65	·3350	·3342	— 8
151·65	·3309	·3303	— 6
163·8	·3240	·3233	— 4
187·9	·3104	·3101	— 3
206·35	·2998	·2998	0
221·35	·2899	·2915	+16
229·2	·2850	·2871	+21
234·3	·2811	·2843	+32
238·9	·2781	·2817	+36
243·1		·2793	

From the above differences it will, I think, be concluded that there is considerable curvature of the “diameter” in the case of ethyl alcohol, and with methyl alcohol it would be still more marked.

I now give a revised table of the critical densities and volumes of the twelve substances, adding, for the sake of convenience, the critical temperatures and pressures. The critical densities are those calculated by M. Mathias ; but in the case of the alcohols I give also the values which I have

Critical Constants.

Substance.	Temperature, Cent.	Pressure, in millims.	Density.	Vol. of 1 gram.	Mol. Vol.	Ratios of Mol. Vol. to that of Fluorbenzene.	
						New.	Old.
Fluorbenzene	286.55	33910	.8543	2.822	270.4		
Chlorobenzene	360	33910	.8661	2.731	306.5	1.133	1.125
Bromobenzene	397	33910	.4857	2.059	322.4	1.192	1.180
Iodobenzene	448	33910	.5838	1.713	348.4	1.289	1.277
Benzene	288.5	36395	.8037	3.293	256.3	.948	.944
Carbon Tetrachloride	283.15	34180	.5558	1.799	276.1	1.021	1.010
Stannic Chloride	318.7	28080	.7423	1.347	349.3	1.292	1.290
Ether	194.4	27060	.2631	3.801	280.7	1.038	1.047
Acetic Acid	321.6	43400	.8514	2.846	170.3	.630	.630
Methyl Alcohol. M.	240.0	59760	.2784	3.592	114.7	.424	.440
" " Y.	"	"	.2705	3.697	118.0	.437	
Ethyl Alcohol. M.	243.1	47850	.2793	3.580	164.3	.608	.620
" " Y.	"	"	.2750	3.636	166.9	.617	
Propyl Alcohol. M.	263.7	38120	.2778	3.600	215.5	.797	.800
" " Y.	"	"	.2752	3.634	217.6	.805	

obtained by the same method, taking into account the curvature of the "diameter." The critical volumes of a gram and molecular volumes are calculated from the densities. The last two columns contain the ratios of the new critical molecular volumes to that of fluorbenzene, together with the ratios given on p. 184 of my previous paper and obtained by the graphical method there described. It will be seen that these ratios show satisfactory agreement.

As regards the alcohols it will be noticed that, if the curvature of the diameter is taken into account, the critical densities are lower and the volumes higher; also that the ratios of the critical molecular volumes to that of fluorbenzene agree better with those obtained by the graphical method.

It may be pointed out that if the generalizations of Van der Waals were strictly true, the angular coefficients (α) of the diameters of different substances should be directly proportional to their critical densities and inversely proportional to their absolute critical temperatures, or that for any substance

$$\alpha = \text{const.} \times \frac{D}{T}; \text{ or } \frac{\alpha T}{D} = \text{const.}$$

I have calculated the values of this "constant" for the substances mentioned in this paper (with the exception of methyl and propyl alcohol) and for the five esters studied by Mr. G. L. Thomas and myself.

Substance.	$\frac{\alpha T}{D}$.	Substance.	$\frac{\alpha T}{D}$.	Substance.	$\frac{\alpha T}{D}$.
Fluorbenzene	·932	Carbon Tetrachloride	·899	Methyl Formate...	·997
Chlorobenzene	·953	Stannic Chloride . .	·988	Methyl Acetate ...	1·047
Bromobenzene	·957	Ether	·972	Ethyl Formate ...	1 061
Iodobenzene	·957	Acetic Acid.....	·993	Ethyl Acetate	1·055
Benzene	·921	Ethyl Alcohol*	1·030	Methyl Propionate	1·021

It can hardly be said that there is more than a rough approximation to constancy in the values of $\frac{\alpha T}{D}$.

I have recalculated the ratios of the actual to the theoretical critical densities, and the results are given in the following table :—

* M. Mathias' value of α .

Fluorbenzene	3·79	Stannic Chloride	3·75
Chlorobenzene	3·78	Ether	3·82
Bromobenzene	3·81	Methyl Alcohol	4·52
Iodobenzene	3·79	Ethyl Alcohol	4·02
Benzene	3·71	Propyl Alcohol	4·02
Carbon Tetrachloride.	3·66	Acetic Acid	5·00

The first eight numbers agree fairly well; and it may be stated that *for many substances the ratio of the actual critical density to the theoretical density (for a perfect gas) is about 3·8*. The alcohols, notably methyl alcohol, and acetic acid, form exceptions to this law, and in the case of the esters the ratios (3·89 to 3·95) are rather high.

VII. *On the Boiling-points of different Liquids at Equal Pressures.* By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol*.

EARLY in the present year, M. E. Colot (*Compt. Rend.* cxiv. p. 653) described a relation between the boiling-points of any two liquids under equal pressures, which may be shortly described as follows.

If t and θ are the temperatures of the two substances at any pressure, then

$$t = A\theta + B,$$

where A and B are constants depending on the nature of the liquids.

The constants given by M. Colot refer to Centigrade temperatures, but for the purpose of this paper it is better to employ absolute temperatures. In this case A remains unaltered, but B has a different value.

There are certain cases in which $B=0$ (for absolute temperatures), and the equation then becomes

$$t = A\theta \text{ or } \frac{t}{\theta} = A.$$

This is identical with the equation given by Dr. Ramsay and myself (*Phil. Mag.* Jan. 1886, p. 33) for certain closely related substances such as ethyl chloride and bromide or chlorobenzene and bromobenzene, and I have shown that it holds good for the four halogen derivatives of benzene.

* Read October 28, 1892.